Influence of production conditions on the yield and environmental stability of biochar

INFLUENCE OF BIOCHAR PRODUCTION CONDITIONS ON ITS STRUCTURE, PROPERTIES AND ENVIRONMENTAL STABILITY.

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Abstract

Biochar, a solid product of biomass pyrolysis, is a promising concept for climate change mitigation and adaptation, as it can sequester atmospheric CO_2 while improving quality of soil where it is stored. However, for this potential to be realised, it is necessary for biochar to have high environmental stability, i.e., resist various decomposition processes over long time. The main objective of this work has been to relate biochar production conditions to the yield, and properties of biochar, particularly its long-term stability. We used our lab-scale pyrolysis facilities to produce biochar at three temperatures between 350 and 550 °C, from selected feedstock (pine, mixed larch and spruce chips, hardwood pellets). We measured the yield of biochar and then used an accelerated ageing assay to obtain information on the stability of biochar. Such information is very important for the assessment of the climate change mitigation potential of biochar, as it has not yet been clearly defined what proportion of biochar actually remains "permanently" sequestered and how much is released back to the atmosphere in the short to medium term. The results of this work showed that despite increase in the stability of biochar with increasing pyrolysis temperature, the yield of stable biochar fraction is nearly independent of the temperature. These findings are essential for the optimisation of pyrolysis conditions for production of biochar with selected properties, as well as for modelling biochar systems and their climate change mitigation potential as compared to other uses of biomass, such as bioenergy, biofuels and/or chemicals.

KEY WORDS: biochar, pyrolysis, stability, CO_2.

1. Introduction

Biochar is a carbon-rich solid product of thermal stabilisation of organic matter created for safe and potentially beneficial storage in soil. It differs from other solid products of thermochemical conversion in that long-term carbon storage is an objective, rather than creation of feedstock for processing industries or fuels such as charcoal, coke and activated carbon.

This distinctly new use of the material presents a number of requirements and challenges that are different from its other (more traditional) uses. In particular it is necessary to ensure that biochar produced from a particular feedstock by any given technology is at least environmentally benign, or even has positive effects (e.g., on plant growth, soil structure, water management etc.). The current state-of-the-art knowledge on biochar and its interaction with the environment has recently been reviewed by Sohi et al.[1] and Lehmann and Joseph [2]. In addition to its environmental impact, biochar must also be highly stable to ensure long-term carbon sequestration. The global potential for sustainable global biochar deployment has been recently analysed by Woolf et al.[3] , results showed that net emissions of GHGs could be reduced by as much as 1.8 Gt CO_2 – C equivalent per year (i.e. 12% of current anthropogenic emissions). Furthermore, potential benefits and risks of biochar were assessed in a report to the UK Department of Energy and Climate Change (DECC)[4]. This report, besides analysing the potential for biochar deployment in the UK also discusses benefits and issues of biochar deployment. It particularly highlights the need to better understand the economics of "pyrolysis biochar systems" (PBS) and the long term stability of biochar.

As there are currently no commercially operating biochar production systems it is very difficult to assess the economics of PBS and a number of assumptions need to be made. One key missing set of information for techno-economic analysis of PBS is the lack of systematic and comprehensive data on pyrolysis product distribution (and energy content), especially for slow pyrolysis systems. Brownsort [5] conducted a broad review of product distribution data for three types of biomass pyrolysis systems (i.e., slow, intermediate and fast pyrolysis) and concluded that in nearly all cases (especially for pilot-scale and larger systems) not all product streams were adequately characterised; this makes analysis of mass and energy balance very difficult, often relying on assumptions. However, this kind of information is crucial, as it is a prerequisite for any analysis of PBS economics and LCA. These techniques are helpful to guide decision making as to where

biochar deployment makes the most sense compared to other options of using biomass, such as direct combustion for power generation, biofuels and chemicals.

Besides the economics of PBSs, it is important that biochar, produced by any particular system, is stable, as stability in the order of centuries is required for biochar to make a meaningful contribution to climate change mitigation [4]. In this respect it is similar to geological sequestration of CO_2. As yet, there is no agreed methodology for determining the long-term stability of biochar and this is a major weakness in the case for carbon storage in biochar. Different approaches have been proposed, including NMR analysis [6] or proximate analysis using the fixed carbon as a measure of stability [7]. These approaches, however, have several drawbacks, such as a small relevance to the environmental processes whose decomposition impacts they are trying to measure, as well as complexity and cost in case of NMR. Various observations regarding biochar stability have been made in the literature; however, most rely on indirect evidence for biochar longevity [2,8-12]. At the UKBRC we have been developing a toolkit that aims to address the issue of long-term stability analysis by subjecting biochar to accelerated aging using different oxidative treatments; this is considered to be more representative of the degradation processes to which biochar would be subjected in the environment. We then used these techniques to analyse a set of chars prepared under different conditions and the main objective of this study was to assess the impact of production conditions on biochar stability.

2. Experimental

The raw materials used in our experiments were pine wood chips (Pine), mixed larch and spruce wood chips (MLS) and hardwood pellets (WP). Moisture content of the feedstock was measured at 43% for Pine, 30% for MLS and 6% for WP (loss on drying, 105 °C, 48h).

The pyrolysis apparatus used, shown in Fig. 1, is a fixed-bed reactor comprising a borosilicate glass sample tube (50mm i/d) with a sintered glass plate at the base. The sample tube is sealed into a porcelain work-tube heated by an electrical split-tube furnace (Lenton, model PSC 12/90/900V) with cascade control of temperature based on a thermocouple within the test sample. Inert gas (nitrogen) is supplied to the work-tube at a controlled rate and, after preheating in the bottom part of the reactor, it passes up through the sample carrying volatiles and syngas into a condenser train.

The train consists of two parts; first the gas passes through a heated filter (170±15 °C) where any entrained particulates are separated, as well as some heavy tars. Second, the particulate-free gas passes through an air condenser with ambient-temperature receiver and two cold traps maintained at -50 to -30 °C using liquid nitrogen cooled acetone. The non-condensable gases leaving from the second trap are vented through a volumetric gas meter (Ritter, TG5), so that the flow rate as well as total flow can be monitored. Differential pressure over the sample bed and gauge pressure at the reactor head are also monitored.

In a typical pyrolysis experiment a biomass sample (approx. 100g) was charged to the sample tube before assembling the apparatus. Pressure sensors were zeroed and the reactor was purged with nitrogen before establishing a steady flow rate of nitrogen as carrier gas; an inlet flow of 0.33 l min^{-1} was used giving a calculated linear cold flow velocity within the empty reactor tube of 3 mm s^{-1}. An outlet gas volume totaliser reading was taken before and after each experiment allowing the volume of syngas produced to be estimated by subtraction of the calculated total carrier gas flow over the same time period.

The sample was heated at an average heating rate of 8 °C min^{-1} to the required hold temperature (350, 450 and 550 °C); the control program usually used a short dwell period just before reaching the hold temperature to avoid overshoot (5-10 min at 10-25 °C below hold temperature). The hold temperature was maintained for 60 minutes before the heating was stopped and the sample cooled naturally, generally cooling to below 100 °C in one hour.

Throughout each experiment sample temperature, reactor pressure, differential pressure and outlet gas flow were monitored and logged. Exothermic events with corresponding gas evolution were observed at different temperatures for the different materials, typically including events around 330-370°C and 390-440°C. In general, the rate of gas evolution subsided soon after the hold temperature was reached to leave steady flows, only slightly raised above the carrier gas flow.

Product yields are given as recovered yields expressed as percent by weight of dry feed. Not all solid and liquid products could be recovered from the apparatus; handling losses were estimated at 5-10% in total.

Syngas product volume was determined from the calculated gas volume derived from the totaliser readings and the carrier gas flow.

Removal of char from the sample tube allowed separation of the main char product from a few percent (1-4%) of 'secondary char', a glassy, brittle char formed by condensates deposited onto the upper part of the sample tube. Tars collected in the hot trap were dark and viscous, almost solidifying when cold. The main liquid fraction collected in the ambient receiver was two-phase, a pale-yellow/orange aqueous phase separating above a heavy, dark-brown oily phase. Only small quantities of condensable products were collected in the cold traps.

The resulting biochar was analysed for labile and stable carbon using tools from a biochar assessment toolkit developed at the UK Biochar Research Centre. Labile carbon was determined using the assay described in [13], where labile biochar carbon was determined using CO_2 evolution from a two week incubation of biochar in a "model" soil under conditions conducive to microbial activity (i.e. optimal temperature and soil moisture contents). Stable carbon was determined using an accelerated ageing assay. This assay involved the thermal and chemical oxidation of milled biochar samples. Accelerated ageing using oxidation was used given that degradation of biochar in soils is a typically oxidative process. Samples were placed in 5% hydrogen peroxide and heated to 80 °C, and carbon stability then was calculated gravimetrically using the %C data of samples before and after oxidation.

3. Results and discussion

The distribution of pyrolysis products is sensitive to the feedstock, as well as production conditions. Figure 2 shows the distribution of solid, liquid and gaseous products from the pyrolysis of WP, MLS and Pine at holding time of 60 minutes at peak temperature, as obtained in our experiments. There were two types of solid products generated by our pyrolysis process and it has been decided to consider them separately, due to their different nature. The first type is the product obtained as the carbonaceous solid residue of biomass particles pyrolysis and is referred to as "char" or "biochar". The second type is referred to as "secondary

char" and it is the solid product of secondary vapour-phase pyrolysis reactions, condensed at the inner surface of the reactor tube. The secondary char is glassy in appearance and unlike biochar it cannot be easily recovered from the reactor tube and, therefore, will not be further discussed in this paper.

A number of trends can be clearly identified in the data shown in Fig. 2, irrespective of the feedstock. With increasing temperature, the yield of liquid and to lesser extent gaseous products increases and consequently the yield of the solid product, i.e. biochar, decreases considerably (approx. 10% points) between 350 °C and 550 °C.

These changes in the product distribution naturally have an impact on the energy distribution between the different carriers, i.e. solids, gases and liquids. With increasing temperature, more and more of the total chemical energy in products is contained in pyrolysis gases and liquids, rather then being retained in the solid. This means that more energy could potentially be generated by utilising the liquid and gaseous product streams in power and/or heat generation processes within a PBS, thus providing additional revenue streams and improving the feedstock use efficiency.

Besides the distribution of the pyrolysis products, their properties are also very important, as the quality of the different product streams determines their possible use. In this work we focussed primarily on the solid products of biomass pyrolysis and will, therefore, cover this aspect in more detail in the following sections, while leaving the liquid and gaseous products aside.

3.1 Char Yield

Figure 3 shows more details on the yield of biochar as a function of temperature, as well as the carbon content of biochar produced under the different conditions. It can be seen that the yield of biochar decreases with the peak pyrolysis temperature in the studied range. This is due to the more severe pyrolysis conditions that enhance the biomass decomposition. The carbon content of biochar, on the other hand, follows the opposite trend to biochar yield, increasing considerably with pyrolysis temperature, as more and more O, H and N is released in the gaseous and vapour phase. To a certain extent this increase in C concentration offsets the decreasing trend in biochar yield and therefore, even though the actual yield of carbon, calculated from

the biochar yield and its carbon content (also shown in Figure 3) decreases with temperature, the decrease is considerably less dramatic than that of biochar yield.

As the primary objective of biochar is to store carbon, it is the yield of carbon contained in the solid product that is important, rather than the yield of the solid product (biochar) itself. Thus, reporting experimental results from pyrolysis experiments aimed at biochar production only in terms of biochar yields without data on carbon yields is not sufficient as it does not provide a true picture of the effectiveness of the process in terms of carbon sequestration potential.

Furthermore, besides the yield of carbon in solid pyrolysis products, it is also necessary to know what portion of this carbon would be stable over periods long enough to make it relevant to climate change mitigation, i.e. the true carbon sequestration potential it provides.

3.2 Stable Biochar Fraction

It is important to determine how much of the carbon contained in biochar is potentially stable over long periods of time as there are likely to be various fractions, differing in their stability, ranging from very unstable (labile) fractions to very recalcitrant (stable) fractions.

Here, it is also important to say that the stability of the carbon is likely to be dependent on the degradation processes and conditions that it is exposed to when sequestered. As the most commonly considered destination for biochar sequestration is soil, the degradation processes to which biochar would be exposed include numerous physical, chemical and biological processes occurring in soils. This is one of the main reasons why we decided to develop and deploy our own methods for assessing biochar stability, to better reflect this situation, rather than using simple measures of biochar stability such as proximate analysis (fixed carbon)..

Figure 4 shows the results obtained from analysis of the biochar samples using our accelerated aging technique. It can be seen that the fraction of recalcitrant carbon in biochar increases with increasing pyrolysis temperature. This means that biochar exposed to higher pyrolysis temperatures contains a higher proportion

of the stable fraction than biochar produced at low temperatures suggesting that from a carbon sequestration point of view, high temperature pyrolysis biochar is preferable.

However, as with concentration of carbon in biochar, which increased with temperature while the yield of carbon decreased (see Fig. 3), similar assessment needs to be made also for the stable fraction of biochar; it is, after all, the yield of the stable fraction that is important rather than merely its concentration in biochar. Figure 4 also shows the yield of stable biochar fraction as determined from our experimental results. It shows that despite the concentration of the stable fraction in biochar dramatically increasing with temperature, the pyrolysis temperature affects the yield of the stable fraction to a much smaller extent (at least for MLS and Pine). These results indicate that from the point of view of sequestering maximum amount of carbon per unit of feedstock, low-temperature conversion processes might perform as effectively as higher temperature pyrolysis processes.

This finding has an important consequence, as it impacts on the economics of the pyrolysis biochar system which would require parallel revenue streams to that from carbon sequestration (due to very low price of carbon), such as power or heat generation and agricultural benefits (e.g. improved crop yield/health, reduced fertiliser use, improved water management, etc.). The first requirement places certain constraints on the quality and quantity of the gaseous and liquid product streams, while the second requirement places constraints on the properties of biochar, particularly those affecting its function in soil, such as ash content (nutrient supply and pH modification), pore structure and size distribution (water retention and holding capacity, surface activity (sorption of nutrient ions), etc. [14]. These demands mean that biochar production processes will need to be set up to maximize the overall benefit, not only the yield of stable biochar, and will therefore be very case specific. The relative independence of the stable carbon yield on pyrolysis temperature would then mean that the production conditions could be set up to maximise other benefits without considerably sacrificing the carbon sequestration potential.

3.3 Non-stable Biochar Fraction

As highlighted in the previous section, the stable fraction of biochar is one of the key parameters to be considered in defining biochar production conditions. However, the non-stable fraction is also very

important, for at least two reasons. First, the labile fraction that evolves from biochar during its storage in soil is highly likely to impact on microbial activity, and therefore affects the functioning of the soil as a whole, including the balance of indigenous labile pools [15]. Second, the non-stable fraction, particularly its less labile part could potentially be further stabilised and, therefore, contribute to increased yield of the stable biochar fraction.

Using our toolkit, we have defined two types of non-stable biochar; first, the so called "labile" fraction is the part of biochar that is released by predominantly microbial activity within the first few weeks or months after the application of biochar to soil and it presents the least stable (most easily degradable) portion of biochar. It is yet unclear which of the constituents of biochar constitute this category, but it is clear that the labile component is only a minor fraction of biochar (unpublished results).

The second type, the so called "semi-labile" fraction is the part of biochar with stability in the range of years to decades, which is composed of more recalcitrant compounds, i.e. those not easily metabolised by soil micro organisms. This fraction presents a significant portion of biochar and is, therefore, of considerable interest. As is the case for the labile fraction, it is not yet clear which chemical constituents of biochar are represented in this category and it will be a subject of future investigation. The substantial yield of the semi-labile fraction makes its composition of considerable importance and interest as it may be possible to further stabilise at least some parts of the semi-labile fraction, thus increasing the yield of the stable fraction and consequently the carbon storage potential of biochar.

4. Conclusions

The main objective of this work was to relate biochar production conditions and feedstock to the yield and properties of biochar, particularly its long-term stability. The results show that yield and properties of biochar are strongly affected by pyrolysis conditions:

i) The yield of biochar decreased considerably with pyrolysis temperature in the range from 350 °C to 550 °C for a holding time of 60 min.

ii) The yield of stable carbon showed only minor dependence on the pyrolysis temperature, despite the increase in concentration of the stable carbon in the biochar with increasing temperature.

iii) The non-stable fraction of biochar consists predominantly of semi-labile carbon with the labile carbon presenting only minor fraction.

iv) Despite its low yield, the labile fraction can play an important role in application of biochar, as it is likely to play an important role in soil processes.

The results of this work present new insights into the interactions between production conditions, biochar yield and its properties. These may prove essential to further optimisation of pyrolysis conditions for production of biochar with selected properties, as well as for modelling biochar systems and their climate change mitigation potential.

5. Acknowledgments

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Figure 1 – Schematic of the fixed-bed pyrolysis apparatus.

Figure 2 – Pyrolysis product yields as a function of temperature.

Figure 3 – Concentration and yield of char carbon as a function of temperature.

Figure 4 – Concentration (empty symbols) and yield (solid symbols) of stable biochar fraction as a function of temperature.

Figure(s)

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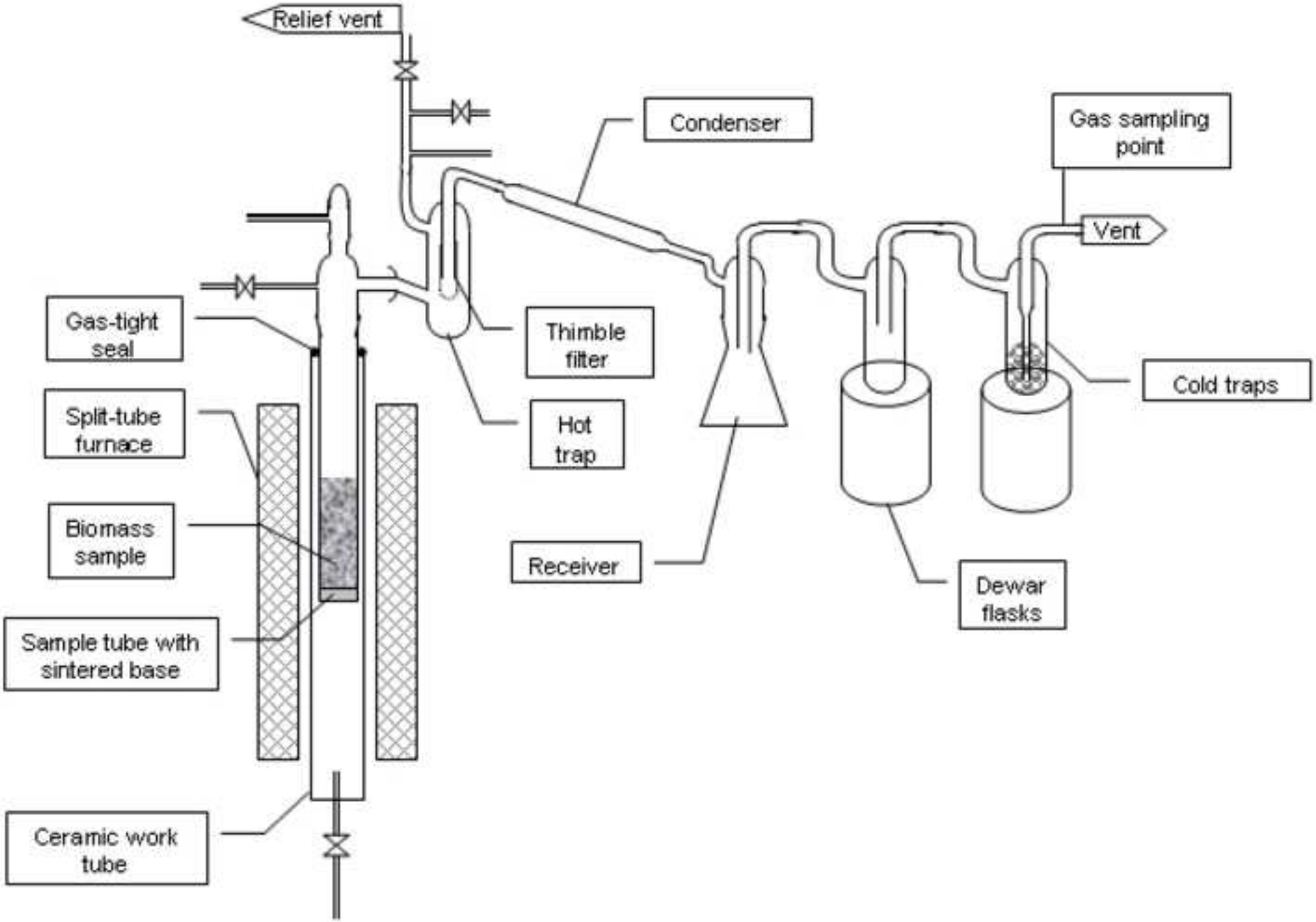

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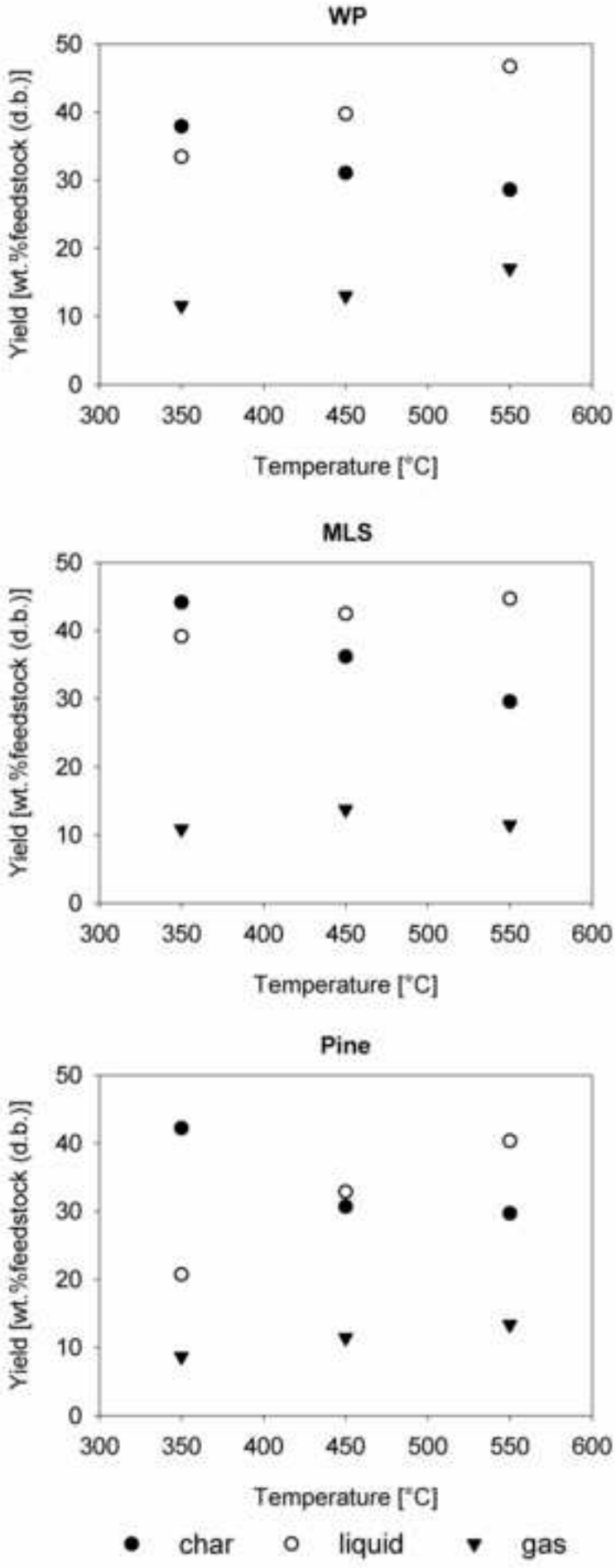

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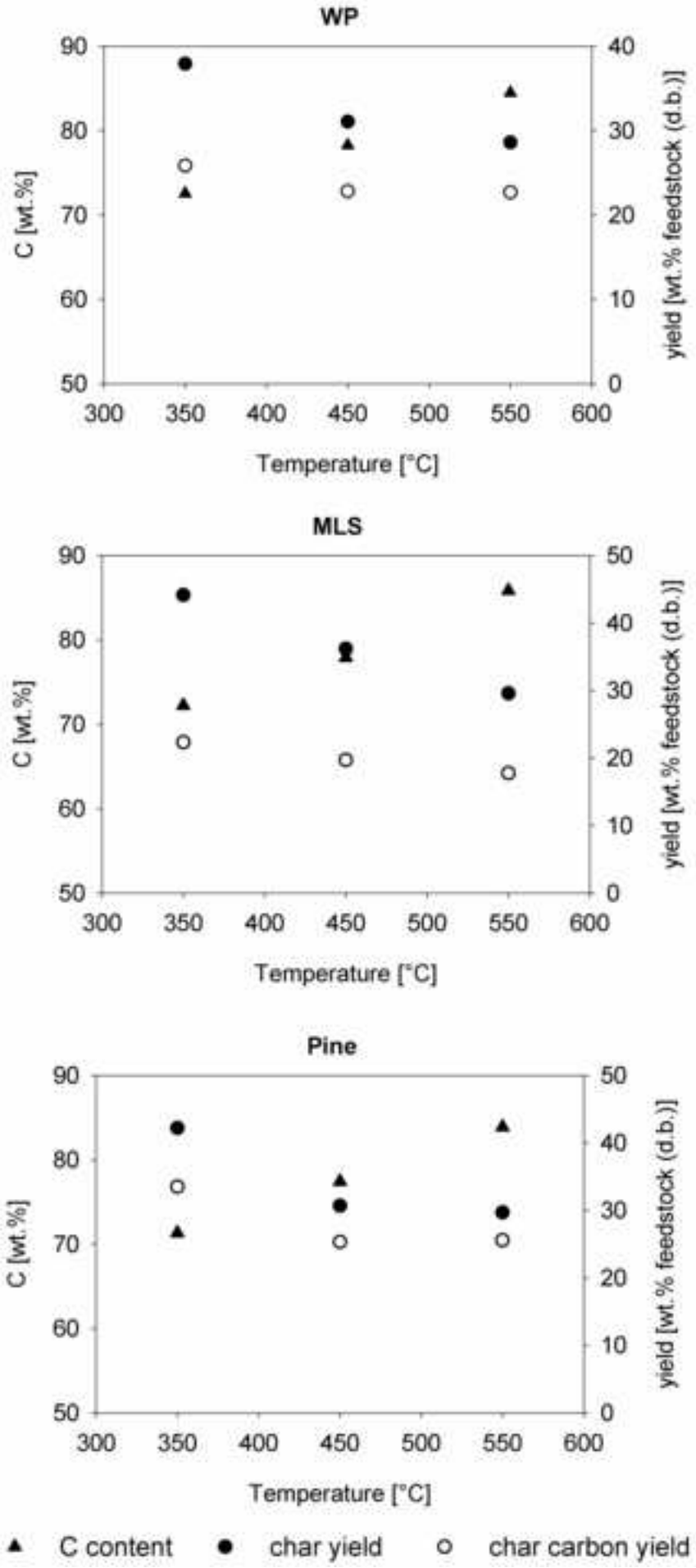

Figure 4

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